



Catalytic reforming of activated sludge model compounds in supercritical water using nickel and ruthenium catalysts

Pooya Azadi, Elie Afif, Hooman Foroughi, Tingsong Dai, Faraz Azadi, Ramin Farnood*

Department of Chemical Engineering and Applied Chemistry, University of Toronto, Canada M5S 3E5

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ABSTRACT

We report the catalytic supercritical water reforming of model compounds of activated sludge at 380 °C using Raney nickel, Ni/ α -Al₂O₃, Ru/C, and Ru/ γ -Al₂O₃ catalysts. The model compounds were glucose, glycine, glycerol, lauric acid and humic acid, representing carbohydrates, proteins, alcohols, fatty acids and humic substances, respectively. Using Raney nickel as the catalyst, the carbon conversions decreased with the following order: glycerol > glucose > glycine > lauric acid > humic acid. The conversion generally increased with reduction in the number of C–C bonds presented per unit mass of the molecules, except for the glycine that contains a nitrogen atom in its structure. Comparison of the experimental yields of methane with the equilibrium values calculated at the corresponding conversions revealed that, in the presence of Raney nickel, methane is almost at a quasi-equilibrium state. Moreover, using binary mixtures of the above model compounds as feedstock, the interactions between these model compounds were investigated. At low catalyst loadings, the presence of humic acid in the binary mixtures resulted in lower carbon conversions compared to the expected values based on the rule of mixtures. Higher gas yields were obtained from the decomposition of these model compounds compared to an activated sludge feedstock. Addition of sludge ash decreased the gasification yields of glucose and glycerol and increased the yields obtained from glycine. Furthermore, since algae are comprised of lipids, proteins, and carbohydrates, the findings of this study also provide a better understating of the catalytic gasification of such feedstock in supercritical water.

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1. Introduction

Due to the increasing concerns over global warming caused by the anthropogenic greenhouse gas emissions and the decline in the fossil fuel resources, the production of gaseous and liquid fuels from the renewable resources such as biomass and wastes has become an important line of research. Energy generation from the municipal and industrial wastes has the additional advantage of eliminating some of the indirect greenhouse gas emissions associated with the biofuels derived from energy crops, including the land-use change, emissions associated with the production of fertilizers, and the loss of soil fertility.

Activated sludge is a waste by-product of the biological wastewater treatment process. It mostly contains carbohydrates, proteins, fats and humic substances, and up to 98 wt% water. Its disposal accounts for 30–50% of the wastewater treatment plant total operating cost, of which the largest portion is associated with

the sludge drying before its disposal by other means (e.g. landfilling, incineration, etc.) [1,2]. Among several alternatives for the conversion of biomass and wastes to fuels, catalytic supercritical water gasification (SCWG) has shown to have a great potential for the production of combustible gases such as hydrogen and methane from dilute (e.g. <20 wt%) organic feedstock [3,4], which renders it suitable for the gasification of activated sludge [5,6]. The treatment of activated sludge using SCWG technology would eliminate the need for drying and could be a viable method for generating local energy at low costs. In this process, sludge is first fed into a non-catalytic pretreatment vessel operated at a temperature range of 250–400 °C to hydrolyze the biopolymers. Due to the low polarity of water near its critical point [7,8], the inorganic ash of sludge precipitate, and can be easily removed from the solution. Finally, the hydrolyzed feed is injected into a catalytic supercritical water reactor to convert the dissolved organics to a gas mixture primarily composed of hydrogen, methane and carbon dioxide.

Since biomass is a complex mixture of various components, model compounds are commonly used by researchers to provide a better understanding of the upgrading reactions, and to help with the synthesis of catalysts with improved performance for such processes. For example, Minowa et al. [9] used glucose as a model compound to represent the carbohydrates in biomass, and showed

* Corresponding author at: Department of Chemical Engineering and Applied Chemistry, Pulp & Paper Centre, University of Toronto, 200 College Street, Toronto, Ontario, Canada M5S 3E5. Tel.: +1 416 946 7525; fax: +1 416 978 8605.

E-mail address: ramin.farnood@utoronto.ca (R. Farnood).

that due to the fast hydrolysis to its monomeric and oligomeric constituents, the decomposition of cellulose and its monomer, glucose, were essentially the same. Other model compounds used to examine the SCWG of biomass include xylan for hemicellulose [10], glycerol for the triglycerides [11–13], and glycine for proteins [11,14,15], and propylphenol for lignin [16].

In addition, the interactions between various constituents of biomass can be studied using mixtures of representative model compounds. Yoshida and Matsumura [10,17] studied the interactions between cellulose, hemicellulose (xylan), and lignin in SCWG process. While gasification efficiencies of mixtures of cellulose and xylan closely matched the expected values, mixtures of cellulose and lignin sulfonate at low catalyst loading ($0.4 \text{ g}_{\text{catalyst}}/\text{g}_{\text{feed}}$) exhibited strong negative deviations from the expected results [10,17]. The extent of the negative deviation decreased at higher catalyst to feed ratios [10] and the authors concluded that the formation of tarry products from the reactions between carbohydrates and lignin was primarily responsible for the catalyst deactivation which, in turn, resulted in lower gas yields. Moreover, Yoshida et al. [10,17] found that the gasification yield of saw dust was nearly 90% of the predicted value based on the rule of mixtures, implying that native lignin in the wood have different gasification characteristics than the isolated lignins. Lower yields obtained from the gasification of isolated kraft lignin compared to the native lignin in biomass (e.g. bark) was hypothesized to be related to its more condensed structure due to the presence of higher C–C refractory interunit linkages as well as the presence of sulfur in the structure which deactivates the catalyst [18]. Furthermore, Kruse et al. investigated gasification of cellulosic materials in presence of proteins [19,20] and found that addition of proteins or amino acids reduces the gas yields.

The choice of catalyst is an important factor for the SCWG process. Nickel and ruthenium have been found to be highly active for the decomposition of biomass in SCW [4,21–23]. The catalyst support was also shown to have a significant impact on the catalytic activity for SCWG reactions. In a recent study, nickel catalysts supported over $\alpha\text{-Al}_2\text{O}_3$, MgO and carbon nanotube (CNT) were found to exhibit the highest catalytic activities among numerous catalyst supports tested [24]. Also, unsupported Raney nickel catalyst is thus far one of the most active catalysts identified for the SCW decomposition of biomass [18,25]. In our previous work [26], we used the Raney nickel catalyst to gasify a 3 wt% activated sludge feedstock at 380°C in a batch reactor, where a maximum yield of 32 mmol/g sludge constituting 46% hydrogen was obtained. We also found that the amount and the composition of the generated gases did not significantly change after 30 min reaction time.

In this study, we report the catalytic SCWG of five model compounds representing substances commonly found in activated sludge, aiming to provide a better understanding of the behavior of different fractions during SCWG of real activated sludge feedstock. These model compounds were glucose (for carbohydrates), glycine (for proteins), glycerol (for alcohols and partly for glycerolipids), lauric acid (for fatty acids) and humic acid (for humic substances). Raney nickel was primarily used as the catalyst, but the performances of $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$, Ru/C , and $\text{Ru}/\gamma\text{-Al}_2\text{O}_3$ for such reactions were also evaluated. The binary interactions between these model compounds in a mixture were also studied as a function of catalyst loading. Additionally, thermodynamic analysis was performed to determine the extent to which gas species reach equilibrium state during the gasification process. Finally, the results obtained in this study were compared to those of previous SCWG studies using activated sludge as a feedstock. Possible mechanisms are proposed to explain the interaction among various components of activated sludge during the hydrothermal gasification process.

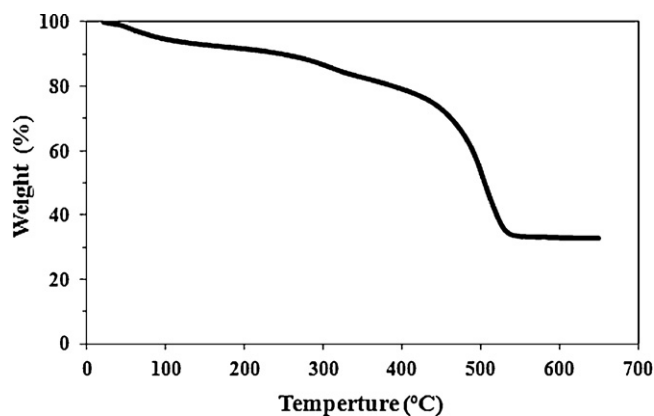


Fig. 1. Thermogravimetric analysis of humic acid.

2. Materials and methods

The experimental setup used in this work consisted of a non-stirred batch reactor made of 316SS with 50 ml volume. For more details about the experimental setup please refer to [26]. Five model compounds were considered in this study: glucose (Sigma–Aldrich), glycine (Mallinckrodt U.S.P), glycerol (ACP Montreal), lauric acid (Sigma–Aldrich) and humic acid (Sigma–Aldrich). Using a 2400 Series II CHNS Analyzer (Perkin–Elmer, USA) operating at the C–H–N mode, the empirical chemical formula of the humic acid was found to be $\text{CH}_{0.5}\text{O}_{0.47}\text{N}_{0.04}$. The ash content of the humic acid was found to be 32% (Fig. 1) using thermogravimetric analysis (TGA Q500, TA Instruments USA). Results of the gasification of humic acid and its mixtures are presented on an ash-free basis. Raney nickel, Ru/C , and $\text{Ru}/\text{Al}_2\text{O}_3$ were obtained from Sigma–Aldrich (Canada), and $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst was prepared by incipient impregnation of $\alpha\text{-Al}_2\text{O}_3$ support (Sigma–Aldrich) with a nickel nitrate precursor, followed by drying at 110°C , calcination at 350°C , and reduction in flowing hydrogen (50 ml/min STP, 30% H_2 , 70% N_2) at 500°C . For each run, 0.3 g of model compounds was added to 9.7 g of deionized water to obtain a total weight of 10 g. The desired amount of the catalyst was then added, and the mixture was loaded to the reactor. The reactor was immersed in a molten salt bath maintained at the 380°C . The molten salt bath consisted of a mixture of potassium nitrate (Alphachem, USA), sodium nitrate and sodium nitrite (General Chemical, USA). This system had a high heating rate (heating time of about 1–2 min) which allowed for reducing the undesirable side reactions that proceed during the heat up time [27]. The corresponding vapor pressure inside the reactor was estimated to be 230 bar. After 15 min, the reactor was quenched to room temperature by immersing into a cold water bath. The final pressure inside the reactor was measured using a digital pressure gauge (Cecomp Electronics, USA), which was subsequently used to calculate the total gas yield. At least one replicate run was conducted for each experiment to ensure that the experimental error are below 10%. The produced gas was collected in a gas bag and analyzed using a Hewlett Packard 5890 Gas Chromatograph equipped with a thermal conductivity detector. Based on the total gas yield and gas composition, the specific yield of each compound was calculated. The thermodynamic equilibrium data was obtained using Aspen Plus process simulator (Aspen Plus, Aspen Technology Inc., USA) based on the Peng–Robinson equation of state. The results of this study are presented in terms of carbon gasification ratio (CGR) and hydrogen gasification ratio (HGR), which are defined as follows:

$$\text{CGR} = (Y_{\text{CH}_4} + Y_{\text{CO}_2} + Y_{\text{CO}})/(\text{mmol C/g feed}) \quad (1)$$

$$\text{HGR} = (Y_{\text{H}_2} + 2Y_{\text{CH}_4})/(\text{mmol H}_2/\text{g feed}) \quad (2)$$

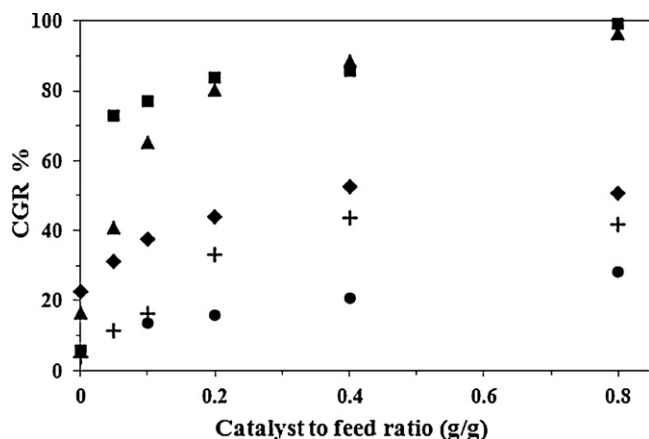


Fig. 2. Carbon gasification ratio (CGR) versus catalyst-to-feed ratio (g Raney nickel catalyst/g dry feed) (380 °C, 15 min, 3 wt% feed), glycerol (■), glucose (▲), glycine (◆), lauric acid (+) and humic acid (●).

where Y_i denotes the yield of gas 'i' in mmol/g of feed on a dry and ash-free basis.

The concentration of each model compound in binary mixtures was set at 1.5 wt%, resulting in a total concentration of 3 wt%. These mixtures were gasified using the procedure described earlier for the individual model compounds. CGR, HGR and the gas yields for the above binary mixtures were also calculated based on the weight fractions of the two compounds and their chemical formula.

To examine the potential effects of inorganic ash on catalytic SCWG of different sludge fractions, 0.075 g of ash, previously obtained from the combustion of activated sludge at 550 °C, was added to the reactor along with the organic feedstock.

3. Results and discussions

3.1. Gasification of single model compounds

Figs. 2 and 3 show the CGR and HGR obtained from the SCWG of single model compounds using different catalyst to feed ratios, respectively. As can be seen from these figures, both CGR and HGR increased with the catalyst loading and approached a near plateau region at about 0.4 g catalyst/g_{feed}, except for the humic acid which continuously generated more gas by increasing the catalyst loading. Also, the HGR of glycerol showed a maximum of 160% at a low catalyst loading before decreasing to a plateau

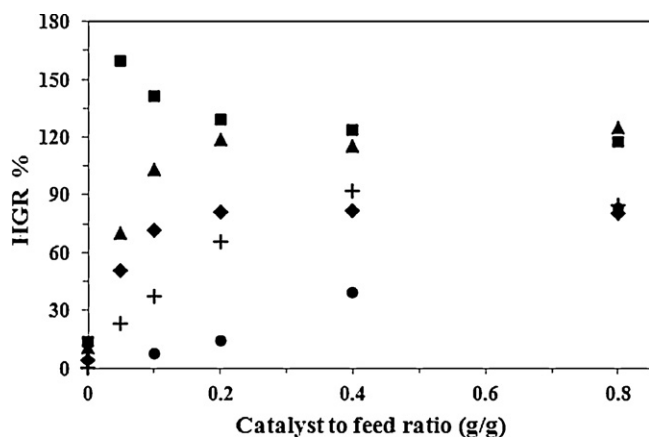


Fig. 3. Hydrogen gasification ratio (HGR) versus catalyst-to-feed ratio (g Raney nickel catalyst/g dry feed) (380 °C, 15 min, 3 wt% feed), glycerol (■), glucose (▲), glycine (◆), lauric acid (+) and humic acid (●).

level of 125%. An HGR of above 100% is due to the production of hydrogen from water molecules through the reforming and water-gas shift reactions. The order of carbon conversion obtained from the decomposition of these model compounds were as follows: glycerol > glucose > glycine > lauric acid > humic acid. These results suggest that carbohydrates (represented by glucose) and alcohols (represented by glycerol) are far more readily gasified using a nickel catalyst compared to proteins, fatty acids and humic substances. These results are consistent with the earlier works [11,19,20] where glycine was found to be relatively hard to gasify and resulted in a loss of yield when added to other model compounds such as glucose. The lower carbon conversions obtained from SCWG of humic acid and lauric acid was likely due to the condensed structure and lack of reactive oxygen functional groups, respectively.

Fig. 4 shows the gas yields obtained from the SCWG of the model compounds using different amounts of Raney nickel catalyst. In general, the trends for the methane and hydrogen yields were similar to those for CGR and HGR, respectively. Furthermore, it is also worth noting that the CO yields in the produced gas were typically less than 1 mmol/g_{feed} and it decreased with increasing the catalyst loading (not shown in this figure).

The primary reaction pathway for the metal-catalyzed decomposition of organics in SCW is shown in Fig. 5. According to this figure, the first step in the decomposition of organics in SCW is hydrolysis in the solution to yield monomers and oligomers (if feedstock was a biopolymer), followed by chemical transformation to other intermediates such as alcohols and acids. The subsequent decomposition of these chemical intermediates on the surface of a metal catalyst through C–C bond cleavage, in conjunction with the water-gas shift reaction, results in the formation of a gas mixture rich in hydrogen and carbon dioxide. In the case of oxygenated biomass compounds, methane can be formed both as a primary and a secondary product, the former of which through the metal-catalyzed cleavage of the C–O bonds of the chemical intermediates and the latter of which through the metal-catalyzed hydrogenation of the produced carbon dioxide. It is therefore expected that the methane yield continuously increases over the course of reaction due to increase in partial pressures of hydrogen and carbon dioxide. Also, the higher the activity of the catalyst to cleave C–O bonds, the higher the rate of methane formation from the primary gasification products (i.e. H₂, CO₂, CO). An increase in methane yield is associated with a decrease in both total gas yield and hydrogen selectivity.

The carbon conversions obtained from SCWG of different compounds versus the specific number of C–C presented in the chemical structure are shown in Fig. 6. As shown in this figure, the carbon conversion generally increased as the number of C–C bonds presented per unit mass of the feed decreased, except for the glycine that contains a nitrogen atom in its structure. These results implied that the cleavage of the C–C bonds was likely preceded at lower rates among all the chemical transformation reactions taking place during decomposition of organic compounds in a SCW medium. More detailed studies are required to determine the effect of C–C bond strengths of different chemical structures on their resistance towards gasification in supercritical water.

3.2. Comparison with the equilibrium yields

Fig. 7 presents a comparison between the experimental results and the calculated equilibrium values for the SCWG of the model compounds, assuming a complete conversion of the feedstock to the gaseous products (i.e. 100% CGR). Expectedly, the gas yields approached the theoretical equilibrium values by increasing the catalyst loading (except for the hydrogen yield from lauric acid). Moreover, the experimental hydrogen yields were significantly higher than the equilibrium yields whereas the experimental

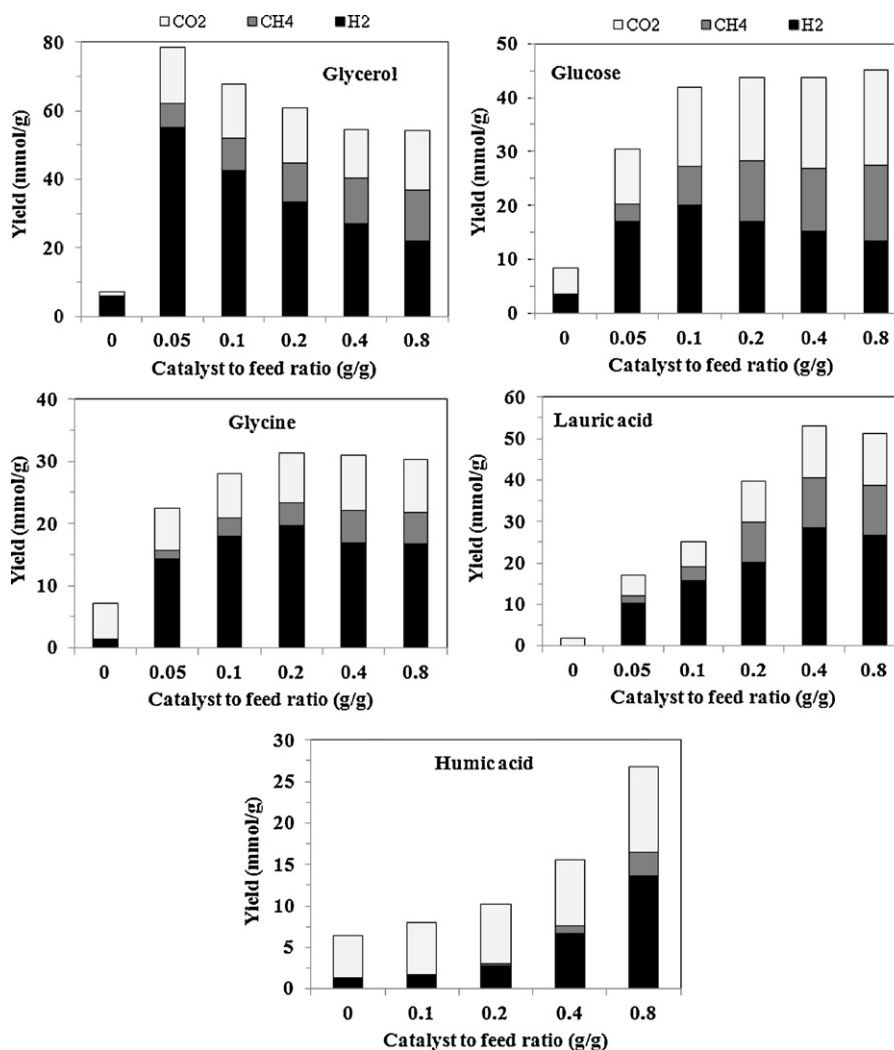


Fig. 4. The gas yields versus catalyst-to-feed ratio for the SCW gasification of model compounds (380 °C, 15 min, 3 wt% feed).

methane yields were always lower than the equilibrium values. In order to evaluate the state of the quasi-equilibrium among the permanent gas species (i.e. H_2 , CH_4 , CO_2 , and CO), equilibrium yields at a carbon conversion equal to the experimental value was calculated and compared to the experimental methane yield (Fig. 8). In order to conduct such calculations, we reduced the amount of organic feedstock according to the experimental CGR values. For example, in order to assess the quasi-equilibrium state among the permanent gas species at a CGR value of 50% that is observed in experiment, we reduced the initial organic loading to half (i.e. 1.5 wt%) of the full load (i.e. 3 wt%). According to this figure, the difference between the experimental yields and that of the equilibrium at the corresponding conversions is relatively small at a high catalyst loading, implying that, in the presence of Raney nickel catalysts and under

the reaction conditions utilized in this work, carbon dioxide and methane are almost at an equilibrium state. Experimental results for methane yield lag the calculated equilibrium conversion values by 7–33%, depending on type of compound. Furthermore, the gap between the experimental and calculated yields decreased by increasing the catalyst loading.

3.3. Binary mixtures of model compounds

In order to determine the extent of the interactions between the model compounds, SCWG of the binary mixtures were studied at two levels of catalyst loadings (Table 1). The parity plots of the experimental versus calculated CGR and methane yields for binary mixtures at low (0.1 g catalyst/g feed) and high (0.8 g

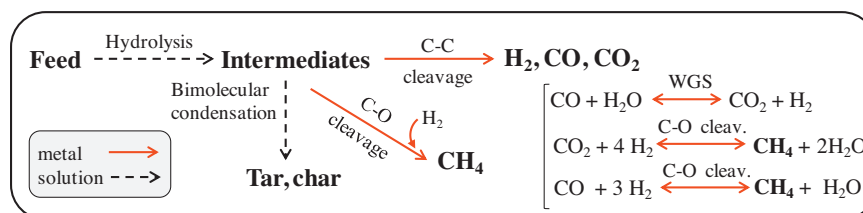


Fig. 5. The primary reaction pathway for the catalytic decomposition of organics in supercritical water [28]. Dashed arrows indicate homogeneous reactions in the solution and solid arrows indicate metal-catalyzed reactions.

Table 1

The experimental results for the gasification of binary mixtures at 380 °C, 15 min, low (0.1 g catalyst/g feed) and high (0.8 g catalyst/g feed) catalyst loadings.

Entry	Feed	Catalyst loading	Yield (mmol/g)			CGR (%)
			H ₂	CH ₄	CO ₂	
1	Glycerol–Glucose	High	17.7	15.2	17.4	100.1
		Low	23.6	9.6	17.3	83.1
2	Glycerol–Glycine	High	17.2	12.8	11.7	83.5
		Low	21.7	7.3	12.9	69.4
3	Glycerol–Lauric	High	44.0	14.7	21.6	80.4
		Low	37.0	6.3	14.6	46.9
4	Glycerol–Humic	High	18.6	11.7	15.4	68.8
		Low	16.7	2.2	9.8	31.1
5	Glucose–Glycine	High	11.0	11.6	13.4	83.8
		Low	11.4	6.8	12.0	62.9
6	Glucose–Lauric	High	23.6	8.1	10.8	44.8
		Low	16.7	3.4	9.4	28.3
7	Glucose–Humic	High	13.4	8.6	13.9	62.4
		Low	6.3	0.9	8.4	24.1
8	Glycine–Lauric	High	37.1	14.3	18.9	72.9
		Low	12.0	3.9	7.5	27.0
9	Glycine–Humic	High	14.2	5.5	10.5	43.8
		Low	4.7	1.0	6.7	21.3
10	Lauric–Humic	High	8.9	3.7	5.8	18.3
		Low	2.1	0.3	1.8	4.1

catalyst/g feed) catalyst loadings are depicted in Figs. 9 and 10, respectively. On these graphs, the larger the distance from the 45° line, the more intense the deviation from the expected values based on the gasification of the individual compounds. At a low catalyst loading, the experimental CGR was consistently lower than the expected values for all the binary mixtures containing humic acid. In contrast, CGR and methane yields for the mixtures of glycerol–glucose, glucose–glycine, and glycerol–glycine exhibited positive deviations from the rule of mixture.

On the other hand, at a high catalyst loading several mixtures exhibited positive deviations from the calculated value (Fig. 10). However, for lauric acid–humic acid mixture, the experimental CGR value was almost half of the calculated value from the rule of mixtures, implying that humic substances were not only difficult to gasify, but also somehow deactivated the catalyst and/or promoted the bimolecular condensation reactions which lead to the formation of stable molecules.

Concerning the gasification of a binary mixture of compounds A & B, the following attributes may cause a deviation from the expected behavior based on their individual behavior under the same reaction conditions.

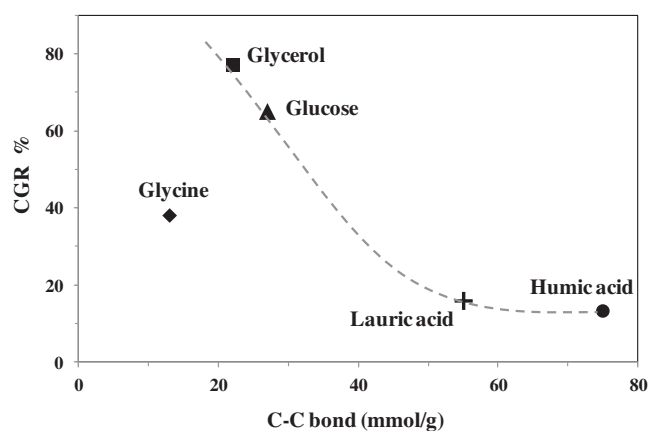


Fig. 6. Carbon gasification ratio (CGR) versus C–C bond in the feed at 380 °C, 15 min, 3 wt% feed, 0.1 g catalyst/g feed. The chemical structure of humic acid was obtained from [29].

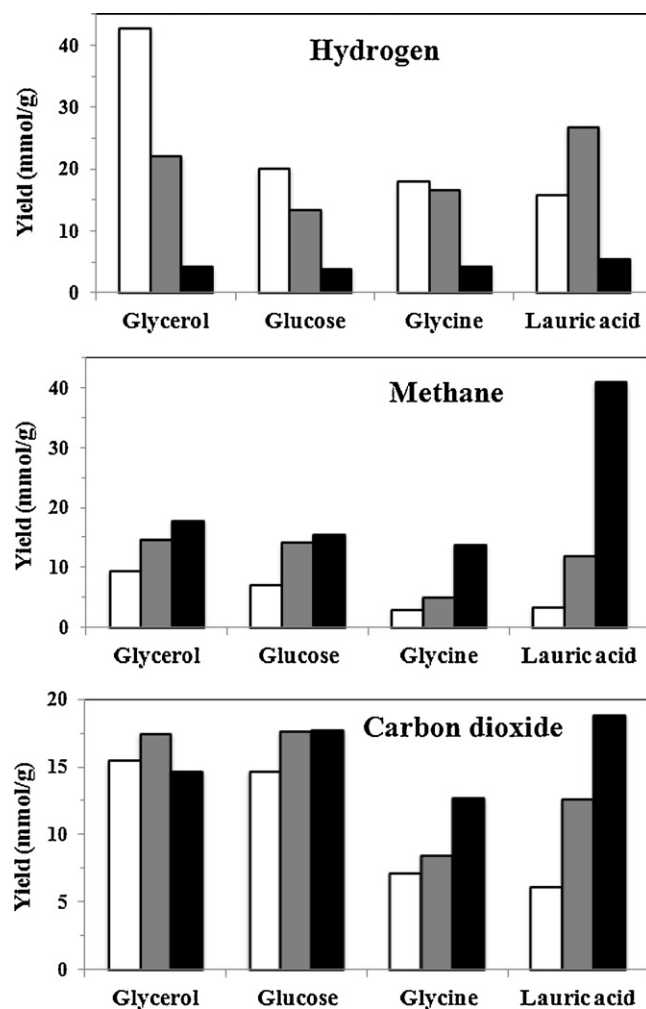


Fig. 7. Experimental yields at 380 °C for low catalyst loading (0.1 g catalyst/g feed, white bars), high catalyst loading (0.8 g catalyst/g feed, grey bars), and the calculated equilibrium yields data at 100% conversion (black bars).

3.3.1. Relative gasification rates of A and B

If the decomposition rate of one of the two compounds in the mixture is substantially higher than that of the other one, the overall gasification yields maybe higher than the predicted values by the rule of mixtures. This is because if the gasification of the fast-reacting compound is completed within the early stage of the reaction, the effective catalyst-to-feed ratio throughout the reaction for the slow-reacting component will increase.

3.3.2. Rates of bimolecular condensation reactions between A–A, B–B and A–B

Considering that the decomposition of tarry materials and char in low-temperature supercritical water medium (e.g. <400 °C) proceeds at very slow rates, the bimolecular condensation reactions in the solution essentially limits the maximum conversion through the formation of stable compounds. The yields of these undesirable products (e.g. tar and char) strongly depend upon the reactivity of the two compounds as well as the reactivity of the chemical intermediates formed during the reactions.

3.3.3. Catalyst deactivation by A, B and reaction intermediates

Catalyst deactivation by A and/or B, or by reaction intermediates decreases the effective catalyst-to-feed ratio and hence, reduces the final gas yields.

3.3.4. Hydrogen produced from the easier-to-gasify compound

A fast production of hydrogen from the easier-to-gasify compound can facilitate the decomposition of the harder-to-gasify compound by enhancing the rates of C–C and C–O bond cleavage, and the desorption of adsorbed intermediates from the catalytic sites.

The overall impact of the abovementioned parameters determines the extent of a negative (or positive) deviation from the predicted values based on the relative amounts of the individual compounds in a binary feedstock.

3.4. Comparison with SCWG of activated sludge

The results obtained from the gasification of the model compounds were compared with those of a sludge feedstock as reported earlier in [26] with and without the addition of catalyst (Fig. 11). In both cases of catalytic and non-catalytic gasification, gas yields obtained from the real sludge feedstock were found to be smaller than those of the model compounds considered in this study. However, we note that the carbon conversion of activated sludge was found to be comparable to that of lauric acid, and was greater than that of humic acid. In order to explain this observation, here we discuss the factors that have possibly caused to obtain higher gas yields from the model compounds. These factors fall into the following three categories.

3.4.1. Inherent gasification rates

The organic content of activated sludge is composed of tens of different compounds which can be generally categorized into four fractions, namely: carbohydrates, proteins, fats, and humic substances. The extent to which one single model compound can represent the behavior of a group of chemical compounds of each fraction varies among the above fractions. For instance, under the reaction conditions used in this study, SCWG of various carbohydrate molecules would essentially result in the same gas yields, independent of the initial molecular weight of feedstock and the type of the carbohydrate (e.g. C₆ vs. C₅) [18]. Therefore, glucose would reasonably represent the behavior of the carbohydrate fraction of activated sludge. On the other hand, it is yet to be determined how well humic acid and glycine can represent the true behavior

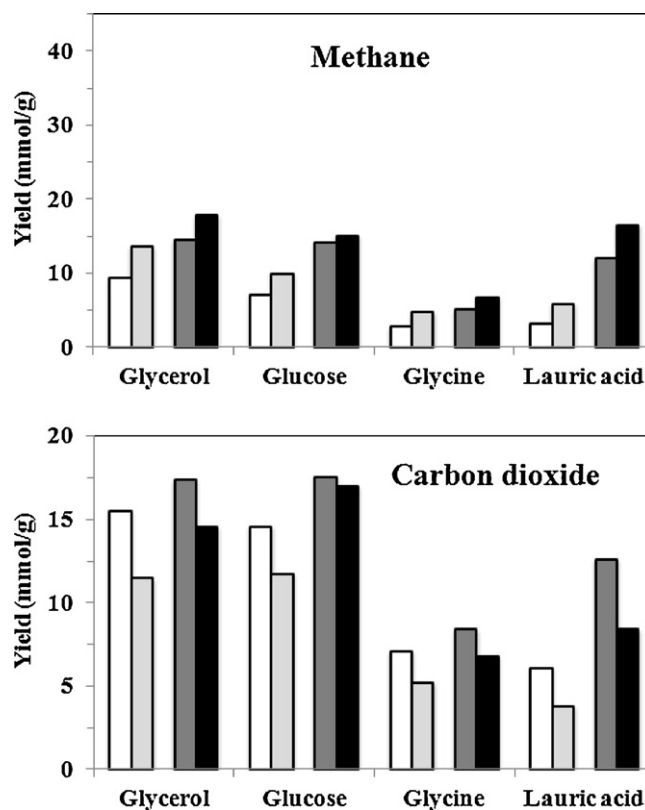


Fig. 8. Comparison of experimental and equilibrium yields of carbon dioxide and methane calculated by assuming a reduced feedstock loading equal to CGR of that experiment. Bars from left to right: experimental yield at low catalyst loading, equilibrium yield at low catalyst loading, experimental yield at high catalyst loading, equilibrium yield at high catalyst loading.

of humic substances and proteins in real sludge feedstock, respectively.

3.4.2. Hydrolysis of activated sludge

Hydrolysis and dissolution of the organics is the first step in the decomposition of activated sludge in a supercritical water medium. Consequently, the hydrolysis rate as well as the final percentage of the dissolved organics would directly affect the gasification of sludge feedstock. Batch hydrolysis of activated sludge shows that less than 45% of the carbon in the feedstock partitioned into the aqueous phase at temperatures in the range of 200–300 °C and hydrolysis times of 10 min [30]. In other words, the easy-to-hydrolyze fractions of sludge such as carbohydrates are dissolved in supercritical water within the first few minutes of the reaction and the reaction temperature, whereas the humic substances and condensed structures may remain insoluble and thus, would not be exposed to the catalytic sites throughout the reaction. Considering that carbon associated with humics and other condensed structures constitutes approximately one third of the total carbon in activated sludge [26], the low hydrolysis yield of these compounds can partly justify the lower yields obtained from the real sludge feedstock compared to the model compounds.

3.4.3. Catalyst poisoning by inorganic ash

It was reported that the presence of sulfur and ash have detrimental effects on the carbon conversion of SCWG of activated sludge [26]. In order to examine the effect of ash on the catalytic SCWG process, we added 0.075 g of ash, which corresponds to a typical ash content of activated sludge (e.g. 25 wt%), to the reaction mixture. The ash sample was prepared by combusting the same activated sludge feedstock that we utilized in our earlier work [26].

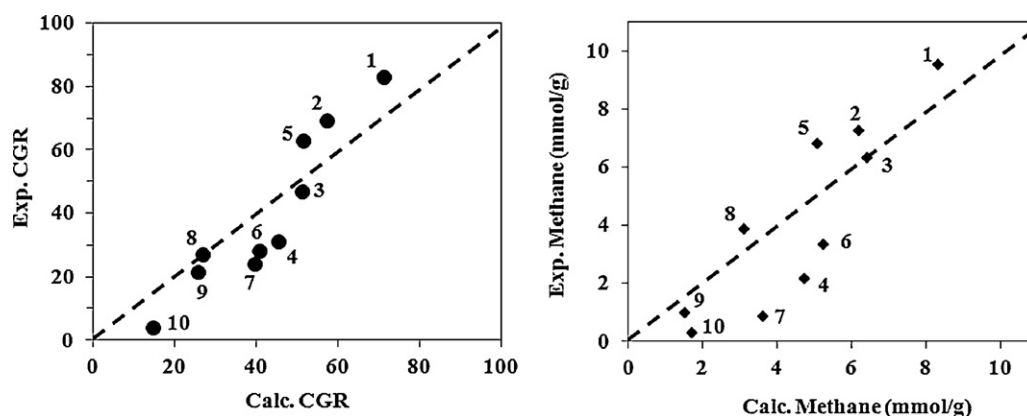


Fig. 9. Experimental versus calculated CGR and methane yields for the gasification of binary mixtures at 380 °C, 15 min and low catalyst loading (0.1 g catalyst/g feed). The numeric labels correspond to the entries in Table 1.

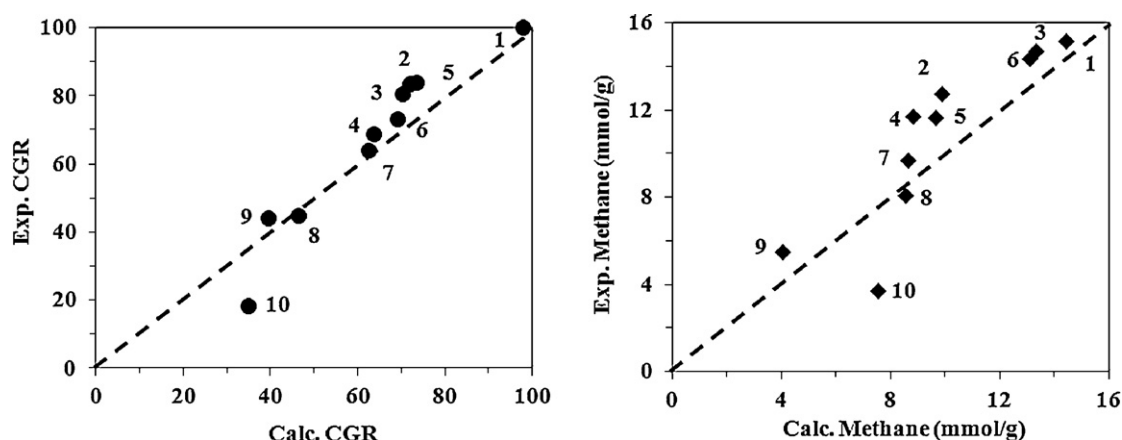


Fig. 10. Experimental versus calculated CGR and methane yields for the gasification of binary mixtures at 380 °C for 15 min and high catalyst loading (0.8 g catalyst/g feed). The numeric labels correspond to the entries in Table 1.

The results of these experiments along with the results of SCWG of sludge and a sludge sample with an additional amount of ash are given in Table 2. It was found that addition of ash to glucose and glycerol decreased the methane yield and carbon conversion, whereas it positively affected the conversion of glycine, and had a negligible effect on the conversion of humic acid. Furthermore, as presented in the row 2 and 3 of Table 2, the addition of extra ash to activated sludge feedstock decreased the carbon conversion by 30%. Considering these results, it can be concluded that the presence of inorganic ash may have also contributed in obtaining lower yields from the activated sludge feedstock compared to the model compounds presented in this study.

3.5. Performances of other catalysts

The gas yields and carbon conversions of the SCWG of sludge model compounds in the presence of Raney nickel, Ni/ α -Al₂O₃, Ru/C and Ru/Al₂O₃ catalysts are given in Table 3. The dispersion of the active metal for these catalysts were reported at 13.4%, 5.0%, 41.0% and 16.7%, respectively [18,24], at an active metal loadings of 93% for Raney nickel, and 5% for Ni/ α -Al₂O₃ and both ruthenium catalysts. Therefore, the number of available active sites for the experiments conducted with Ni/ α -Al₂O₃, Ru/C, and Ru/Al₂O₃ catalysts were 37%, 16% and 7% of that of Raney nickel, respectively. The catalyst-to-feed ratios (i.e. 0.4 Ni g/g_{feed} and 0.02 g Ru/g_{feed}) were

Table 2

The effects of ash addition on gas yields and CGR for the gasification of model compounds and activated sludge [26] at 380 °C for 15 min, 0.8 g catalyst/g feed.

Feedstock	Ash (g)		H ₂ (mmol/g)	CH ₄ (mmol/g)	CO ₂ (mmol/g)	CGR (%)
	Addition	Total				
Sludge	0	0.075	9.8	4.6	7.5	39.7
Sludge ^a	0	0.075	12.6	6.4	8.4	48.7
Sludge ^a	0.075	0.15	13.6	4.2	6.1	33.7
Glycerol	0	0	22.1	14.6	17.4	99.0
Glycerol	0.075	0.075	35.4	12.0	15.6	85.2
Glucose	0	0	13.4	14.2	17.6	96.6
Glucose	0.075	0.075	16.3	11.5	17.1	86.1
Glycine	0	0	16.7	5.1	8.4	50.7
Glycine	0.075	0.075	17.8	5.2	11.2	84.6
Humic acid	0	0	13.5	3.0	10.3	28.2
Humic acid	0.075	0.075	12.2	2.8	10.7	28.8

^a Catalyst loading: 1.1 g/g feed.

Table 3
Comparison of the gasification yields for the model compounds at 380 °C for 15 min using nickel and ruthenium catalysts (catalyst loading 0.4 g Ni/g feed and 0.02 g Ru/g feed).

Feed	Catalyst	Yield (mmol/g)			CGR (%)	HGR (%)
		H ₂	CH ₄	CO ₂		
Glycerol	–	5.8	<0.1	1.2	5.5	13.9
	Raney nickel	27.0	13.4	14.2	85.1	123.7
	Ni/ α -Al ₂ O ₃	23.3	14.9	17.4	99.6	122.1
	Ru/C	12.9	17.8	14.2	~100	111.6
	Ru/ γ -Al ₂ O ₃	10.5	18.0	15.0	~100	106.9
Glucose	–	3.6	<0.1	4.8	16.5	11.2
	Raney nickel	15.3	11.6	16.8	87.5	115.5
	Ni/ α -Al ₂ O ₃	15.3	6.3	15.3	65.7	83.6
	Ru/C	6.4	4.0	11.4	47.6	43.0
	Ru/ γ -Al ₂ O ₃	11.7	3.4	11.7	47.1	55.4
Glycine	–	1.3	<0.1	5.8	22.5	4.4
	Raney nickel	17.0	5.2	8.9	52.6	81.9
	Ni/ α -Al ₂ O ₃	12.8	7.1	8.0	57.3	80.9
	Ru/C	7.6	8.2	6.7	56.3	72.0
	Ru/ γ -Al ₂ O ₃	9.6	8.1	10.9	72.1	77.7
Lauric acid	–	<0.1	<0.1	1.7	3.7	<0.1
	Raney nickel	30.6	12.4	13.3	43.7	92.3
	Ru/C	8.7	7.1	5.2	20.7	38.1
	Ru/ γ -Al ₂ O ₃	18.3	7.5	5.2	21.7	55.4
Humic acid	–	1.3	<0.1	5.0	6.9	5.5
	Raney nickel	6.6	0.9	8.6	20.9	39.4
	Ni/ α -Al ₂ O ₃	2.6	0.1	5.3	11.6	12.4
	Ru/C	0.6	0.3	6.6	14.7	4.5
	Ru/ γ -Al ₂ O ₃	0.3	<0.1	5.6	12.1	1.5

chosen based on the results of preliminary experiments using these catalysts in such way that comparable gas yields are obtained from both types of metals.

The Ni/ α -Al₂O₃ catalyst showed a higher activity than Raney nickel for the decomposition of glycerol and glycine, and a lower activity for the conversion of glucose and humic acid. Considering the low nickel loading (i.e. 5 wt%), the cheap price of the support material, and the superior hydrothermal stability [24], Ni/ α -Al₂O₃ catalyst holds a great potential to be utilized in SCWG processes in the future. It was found that, except for the conversion of glycine, both ruthenium catalysts resulted in comparable carbon conversions. However, considering the catalyst dispersions, the alumina-supported ruthenium catalyst had higher turnover frequency compared to Ru/C. The order of carbon conversion for the ruthenium-catalyzed experiments was glycerol > glycine > glucose > lauric acid > humic acid. Similar to Raney nickel, the ruthenium catalysts were also highly active for catalyzing the methanation reactions.

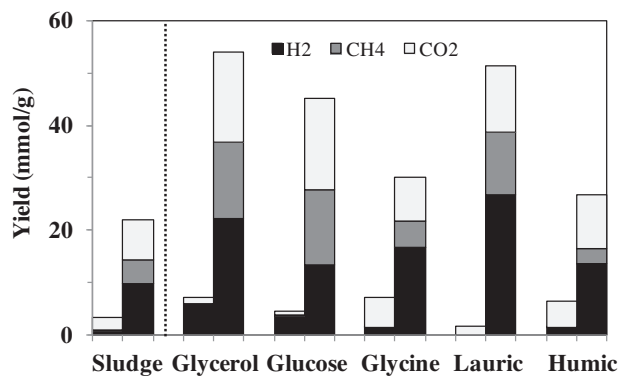


Fig. 11. The gas yields for the SCWG gasification of activated sludge [26] and model compounds, with no catalyst (the left bar for each feedstock) and with 0.8 g/g_{feed} catalyst (the right bar for each feedstock) at 380 °C, 15 min, and 3 wt% feed.

4. Conclusions

In this paper, catalytic SCWG of glucose, glycine, glycerol, lauric acid and humic acid, model compounds of activated sludge, was investigated using a batch reactor. The carbon conversion generally increased by increasing the catalyst loading. The carbon conversion was obtained from decomposition of these model compounds using Raney nickel were as follows: glycerol > glucose > glycine > lauric acid > humic acid. The order of carbon conversion was negatively correlated with the specific number of C–C bonds per unit mass to be cleaved to form permanent gas molecules. Furthermore, the binary interactions between the above model compounds were investigated. It was found that at low catalyst loadings, the presence of humic acid caused a negative deviation from the rule of mixtures and resulted in lower gas yields compared to the expected amounts. At the higher catalyst loadings, however, the methane yield and the carbon gasification ratio more closely followed the rule of mixtures. Results of this study were compared to those previously obtained from SCWG of activated sludge at the same reaction conditions. It was found that the carbon conversion of sludge was lower than those of glucose, glycerol, and glycine, and was higher than the yield obtained from humic acid. Finally, we showed that the presence of inorganic ash decreased the gasification yields of glucose and glycerol, and increased the gasification yields of glycine.

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